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**WO 03/060234 A1**

(54) Title: **BASIC SUSPENSION, ITS PREPARATION AND PROCESS FOR PAPER DEACIDIFICATION**

(57) Abstract: Basic suspension wherein oxides, hydroxides, carbonates, or their mixture, in the form of particles having determined dimensions are suspended in the appropriated solvents, are described. Processes for the preparation of the above said suspensions and of the suspended particles are also described together with the uses of the suspensions in processes for paper deacidification and/or porous materials consolidation.

## BASIC SUSPENSION, ITS PREPARATION AND PROCESS FOR PAPER DEACIDIFICATION

Field of the invention

The present inventions refers to basic suspensions which, thanks to their physico-  
5 chemical properties, can annul the acidity present in papers, which depends on  
the paper production processes, on the environment pollution, and on the usage of  
acid inks as, for example, in the modern books.

State of the art

It is well known how the presence of acidity in paper is the main responsible of its  
10 degradation with consequent loss of a lot of important information and in particular  
of historically important documents.

The acidity, which is present particularly in modern paper, forms during the paper  
manufacture, it is also a consequence of the use of acid inks (which are very  
common especially in the last centuries) or because of the adsorption of acid  
15 pollutants which are present in the air.

Many different techniques and products have been studied or developed in order  
to eliminate acidity from paper and published documents (paper de-acidification).  
Unfortunately, up to now, the problem is far to be satisfactorily solved, and the  
specialists are intensively looking for new products capable of annulling the acidity  
20 present in paper.

Calcium, magnesium, and barium hydroxide aqueous solutions have been widely  
used for many decades, but, unfortunately, they had often induced not desirable  
side effects, because of their strong alkaline conditions, with subsequent  
depolymerization of cellulose.

Non aqueous deacidification processes have also been proposed. In Smith R.D., Mass Deacidification at the Public Archives of Canada in Conservation of Library and Archive Materials and the Graphic Arts, Butterworth Ed., London, 1987 the use of magnesium alkoxide deacidification solutions (Wei T'o method) is described; another method widely used is the Bookkeeper method which is based on the application of suspended MgO that, subsequently converted in magnesium hydroxide, forms the alkaline reservoir. Unfortunately, these methods use chlorofluorocarbon (CFC) solvents. Alternatively, some solvent mixtures have been recently experimented, as triethylene (90%) and methanol, but all of them are harmful.

Despite of its scarce usage, calcium hydroxide is an excellent deacidifying agent. Calcium hydroxide is physico-chemically friendly to most of papers and, once converted to calcium carbonate, works efficiently as alkaline reservoir. In IT 1.286.868 (in the name of the same Applicant) it is reported that suspensions of calcium hydroxide could be used to consolidate mural paintings and to deacidify paper. However, the calcium hydroxide suspensions in organic solvent described in this document were obtained from lime and the particle size distribution was quite broad and larger than several micrometers. Smaller particles were around 0.5 microns, 80% were greater than 1 micron. This originated two problems: firstly, kinetic stability was good but not excellent for some application procedures, for example spraying; secondly, because of particle sizes, a white glaze (or spots) on the treated surfaces could form.

Large calcium hydroxide particles showed a poor adhesions and penetrability into the cellulosic fibres.

Deacidifying agents must ensure good adhesion with fibres, so that the alkaline reservoir acts efficiently. Therefore, according to physico-chemical features of cellulose, particles with a surface charge density are preferred. Both these requirements are ensured by the use of particles smaller than micron size.

5 Summary of the invention

The present invention refers to basic suspension wherein the suspended particles have determined dimensions, moreover the invention refers to process for the preparation of the suspensions and of the suspended particles and to the use of the suspension in processes of paper deacidification and porous materials  
10 consolidation.

Detailed description of the invention

The present invention makes it available basic suspension which allow the overcoming of the problems connected with paper acidity.

The suspension according to the inventions are preferably suspensions of basic  
15 oxides or hydroxides (which are capable of forming carbonates when in contact with the CO<sub>2</sub> of the air or to form, once adsorbed on the treated material, a reservoir of basicity stable for long periods of time) or basic carbonates or their mixture.

Particularly preferred according to the invention are the oxides, hydroxides or  
20 carbonates of alkali or earth-alkali metals or also other analogous compounds having basic properties.

Examples of compounds suitable for the suspensions according to the invention are: Li<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O, MgO, CaO, SnO, SnO<sub>2</sub>, PbO, Pb<sub>2</sub>O, Pb<sub>2</sub>O<sub>3</sub>, BiO, Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, LiOH, NaOH, KOH, Mg(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>, Al(OH)<sub>3</sub>, Sn(OH)<sub>2</sub>, Sn(OH)<sub>4</sub>,

$\text{Pb}(\text{OH})_2$ ,  $\text{Bi}(\text{OH})_3$ ,  $\text{Sb}(\text{OH})_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  decahydro,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{PbCO}_3$ , anhydro and basic,  $\text{Bi}_2\text{O}_2\text{CO}_3$  or their mixtures.

Particularly preferred according to the invention are the suspensions of  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Sn}(\text{OH})_2$ .

- 5 The preferred suspending solvents are chosen in the group consisting of: water, ethyl ether, acetone, alcohols, and their mixtures.

Among the alcohols particularly preferred are: methanol, ethanol, 1-propanol, 2-propanol, butanol, pentanol, and their mixtures.

- Particularly preferred are suspension of the  $\text{Ca}(\text{OH})_2$  hydroxide in 1% (w/w) in  
10 water and 99% in 1-propanol (or 2-propanol).

- The dimensions of the hydroxide particles in suspension play also a crucial role in the suspensions according to the invention. In fact, such particles must be capable of entering the fibres of the materials to treat, linking with them, without covering effect over the written text since this would produce a not desirable aesthetically  
15 effect. Large particles need longer time to penetrate in depth, but the fast volatilisation of used organic solvents does not usually allow it. Therefore, a strict control of particle size is essential before the application.

- Particularly preferred are suspensions according to the invention wherein the suspended particles have dimension comprised between 10nm up to 2 $\mu\text{m}$ , more  
20 preferably between 50nm up to 500nm.

The suspensions according to the invention have a concentration of suspended particles in the solvent preferably comprised between: 0.1-50 g/L more preferably between 1-25 g/L.

Especially preferred is a concentration of: 10 g/L.

The suspensions according to the invention can be obtained by vigorous stirring of the particles to be suspended in the appropriate solvent (or solvents mixture), if necessary with the aid of a sonicator or ultra-sonicator or with the aid of a homogeniser.

- 5 The particles to be suspended, having the desired measures, can be obtained by high temperature homogeneous phase reaction, heterogeneous phase reaction (slaking of oxides), and by mixing two water in oil microemulsion obtaining a low solubility salt in nanosized aqueous core.

The first process consists in reacting solutions of the appropriate reagents (for  
10 example a solution of an hydroxide as NaOH and a solution of a chloride as  $\text{CaCl}_2$ ) at high temperature (about  $90^\circ\text{C}$ ) under stirring.

The solutions to be reacted can be obtained by solving the reagents in a solvent chosen in the group consisting of: water, a solution of diols or a mixture water/diols (the reagents can be solved both in the same or each one in a different solvent  
15 chosen from the above said group).

The preferred diols are  $\text{C}_{1-6}$  alkane diols as, for example, 1,2 ethandiol or 1,2 propandiol.

The suspension obtained after reaction at high temperature and containing the formed particles is cooled down to room temperature under  $\text{N}_2$ , the supernatant  
20 solution is eliminated and the suspension is washed to eliminate secondary reaction products and concentrated in vacuum to form a paste which can be suspended again in the desired solvent amount.

According to the slaking of oxides process the oxide is slaked in pure water, the obtained hydroxide paste is mixed with an alcohol under vigorous stirring and sonicated or homogenised.

Alternatively, according to known techniques, two water in oil microemulsions are prepared wherein the aqueous phase containing salts, when the two microemulsions are mixed precipitation takes place wherein the nanosized dimensions of the aqueous drops impose limited growth of particles.

Given the above said, examples of suspensions according to the invention are reported hereinafter in order to better illustrate the invention:

#### 10 **Example 1**

Calcium hydroxide micro-particles have been obtained by slaking CaO powder in pure water, at room temperature:

- CaO powder 10 g
- Water 30 g

15 Successively, suspensions have been prepared by mixing the calcium hydroxide paste with alcohol, under vigorous stirring, and have been sonicated for 30 minutes with an ultra-sonicator for further reducing the particle size and obtaining a complete dispersion of the calcium hydroxide agglomerates. A homogeniser system, for preparation of some hydroxide dispersions, can also be used.

#### 20 **Example 2**

Calcium hydroxide micro-particles have been obtained by slaking CaO powder in water/alcohol mixtures, according to the following proportions:

- CaO powder 1 g
- Water 5 g

- 1-propanol 25 mL

The metal oxide/water/alcohol mixture, after 30 minutes of sonication or vigorous stirring has been left to rest at least 8 hours. Suspensions have been prepared by mixing the calcium hydroxide paste, after filtration, with alcohol, under vigorous stirring. Suspensions have been sonicated for 30 minutes with an ultra-sonicator for further reducing the particle size and obtaining a complete dispersion of the calcium hydroxide agglomerates. A homogeniser system, for preparation of some hydroxide dispersions, was also necessary.

### Example 3

Calcium hydroxide nanoparticles, from homogeneous phase reaction, have been achieved by mixing a NaOH aqueous solution with a  $\text{CaCl}_2$  aqueous solution. They were previously heated up to a selected temperature (around 90 °C), under continuous stirring and keeping the temperature of the mixture constant within  $\pm 1$  °C; the supersaturating degree was kept in the range 2-10. Aqueous  $\text{Ca}(\text{OH})_2$  suspension was allowed gradually reaching the room temperature under a nitrogen atmosphere to avoid the  $\text{M}(\text{OH})_2$  carbonation. The supernatant solution was discarded and the remaining suspension was washed five times with water to reduce the NaCl concentration below  $10^{-6}$  M. Each time, the dilution ratio between the concentrated suspension and the washing solution was about 1:10. The complete removal of NaCl from the suspension was controlled by the  $\text{AgNO}_3$  test. The suspension was then concentrated in vacuum at 40 °C up to a weight ratio  $\text{M}(\text{OH})_2/\text{water}$  of 0.8, that is the same of the standard slaked lime paste. Dispersions have been prepared by mixing 10g of the calcium hydroxide paste with 1L of alcohol, under vigorous stirring, and/or by using a homogeniser.



**Example 4**

Calcium hydroxide nanoparticles, from homogeneous phase reaction, have been obtained by mixing a NaOH aqueous solution with a  $\text{CaCl}_2$  diol solution (i.e. 1,2 ethandiol or 1,2 propandiol). Diol solution was previously heated up to a selected temperature (around 150 °C), under continuous stirring and keeping the temperature of the mixture constant within  $\pm 1$  °C; the supersaturating degree was in the range 2-10. The NaOH aqueous solution was added dropwise to diol solution keeping the temperature around 150°C. The  $\text{Ca}(\text{OH})_2$  water/diol suspension was allowed gradually reaching the room temperature under a nitrogen atmosphere to avoid the  $\text{M}(\text{OH})_2$  carbonation. The supernatant solution was discarded and the remaining suspension was washed five times with water to reduce the NaCl concentration below  $10^{-6}$  M. Each time, the dilution ratio between the concentrated suspension and the washing solution was about 1:10. The complete removal of NaCl from the suspension was controlled by the  $\text{AgNO}_3$  test. Then, water/diol suspension was washed several times with 2-propanol to remove diol solvents. Successively, solutions were concentrated in vacuum at 40 °C up to a weight ratio  $\text{M}(\text{OH})_2/\text{water}$  of 0.8, that is the same of the standard slaked lime paste. Dispersions have been prepared by mixing 10g of the calcium hydroxide paste with 1L of alcohol, under vigorous stirring, and/or by using a homogeniser.

**Example 5**

Two water in oil microemulsions have been obtained.

$\text{C}_{12}\text{E}_4$  surfactant solutions in cyclohexane have been prepared and used as oil phase in the microemulsion. These solutions have been mixed with NaOH (0.1M) and  $\text{CaCl}_2$  (0.05M) aqueous solution.

Microemulsion (water in oil) composition is:

- $C_{12}E_4$  0.15 g (0.2M)
- Cyclohexane 1.15 g
- NaOH (0.1M) and  $CaCl_2$  (0.05M) aqueous solution 25  $\mu$ L (w=2)

5 Water/surfactants molar ratio ranging (molar ratio w=water/surfactant) from 1 to 5.

Aqueous solution was added to oil phase/surfactant solution by a microsyringe.

The preparation was held at 15°C. Similar isotropic, transparent, and stable systems, were obtained in a wider temperature range, 15-25°C. Microemulsions have been equilibrated at 15°C for 10 days. Crystallization processes took place  
10 within the confined volume of the microdroplets. Synthesized particles, after filtration, washing, and drying have been dispersed in nonaqueous solvents, by vigorous stirring and/or with the aid of a homogeniser.

#### Example 6

Solution of Igepal CO 520 in cyclohexane (0.15M) has been prepared and mixed,  
15 respectively, with an aqueous solution of NaOH (0.5M) and with an aqueous solution of  $CaCl_2$  (0.25M).

Microemulsion (water in oil) composition is:

- Igepal CO 520 solution (0.15M) 1 g
- NaOH (0.5M) and  $CaCl_2$  (0.25M) aqueous solution 25  $\mu$ L (w=2)

20 Water/surfactants molar ratio ranging (molar ratio w=water/surfactant) from 1 to 11.

Aqueous solution was added to oil phase/surfactant solution by a microsyringe.

The preparation was held at environmental (25°C). Analogous systems, isotropic,

transparent, and stable was obtained in a wider temperature range, 15-25°C.

Microemulsions have been equilibrated at 25°C for a week.

Synthesized particles, after filtration, washing, and drying have been dispersed in nonaqueous solvents, by vigorous stirring and/or with the aid of a homogeniser.

5 Procedures for application

The physico-chemical properties of the prepared dispersions make them very attractive for different application procedures in paper deacidification processes, such as:

- spraying,
- 10 • immersing,
- brushing,
- mass-deacidification process.

Small particle dimensions allows using a sprayer without risks of hole occlusion.

The spraying method is preferred.

- 15 The complete immersion of paper sheet is possible also for longer period. Aqueous deacidification methods, because of the strong aggressive effect of high pH, do not allow a long contact with paper sheet, commonly up to 20 minutes. This produces only a poor deacidification effect.

- Moreover the basic suspension's according to the invention can be used also for  
20 the consolidation of porous materials as for example stones, plasters building materials and similar.

**Claims**

- 1) Basic suspension wherein the suspended particles have dimensions comprised between 10nm up to 2 $\mu$ m.
- 2) Basic suspensions according to claim 1 wherein the suspended particles have  
5 dimensions comprised between 50nm up to 500nm.
- 3) Basic suspensions according to claims 1 and 2 wherein the suspended particles are basic oxides or hydroxides or carbonates or their mixture.
- 4) Basic suspensions according to claim 3 wherein the suspended basic oxides are chosen in the group consisting of: Li<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O, MgO, CaO, SnO, SnO<sub>2</sub>,  
10 PbO, Pb<sub>2</sub>O Pb<sub>2</sub>O<sub>3</sub>, BiO, Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub> or their mixtures.
- 5) Basic suspensions according to claim 3 wherein the suspended basic hydroxides are chosen in the group consisting of : LiOH, NaOH, KOH, Mg(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>, Al(OH)<sub>3</sub>, Sn(OH)<sub>2</sub>, Sn(OH)<sub>4</sub>, Pb(OH)<sub>2</sub>, Bi(OH)<sub>3</sub>, Sb(OH)<sub>3</sub> or their mixtures.
- 15 6) Basic suspensions according to Claim 3 wherein the suspended basic carbonates are chosen in the group consisting of: Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> deca-hydro, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, MgCO<sub>3</sub>, CaCO<sub>3</sub>, PbCO<sub>3</sub>, anhydro and basic, Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> or their mixtures.
- 7) Basic suspensions according to Claims 1 – 6 wherein the solvents are chosen  
20 in the group consisting of: water, ethyl ether, acetone and alcohols and their mixtures.
- 8) Basic suspension according to claim 7 wherein the alcohols are chosen in the group consisting of: methanol, ethanol, 1-propanol, 2-propanol, butanol, pentanol, and their mixtures.

- 9) Basic suspension according to Claims 1 – 8 consisting of:  $\text{Ca}(\text{OH})_2$  hydroxide particles suspended in 1% water and 99% 1-propanol or 2-propanol (w/w).
- 10) Process for the preparation of the suspensions according to Claims 1 – 9 by vigorous stirring of the particles to be suspended in the appropriate solvent (or solvents mixture), if necessary with the aid of a sonicator or ultra-sonicator or with the aid of a homogeniser
- 11) Process according to Claim 10 wherein the particles to be suspended are obtained by high temperature homogeneous phase reaction.
- 12) Process according to Claim 10 wherein the particles to be suspended are obtained by slaking of the oxides.
- 13) Process according to Claim 10 wherein the particles to be suspended are obtained by mixing two water in oil microemulsions, giving a low solubility salt in nanosized aqueous core.
- 14) Use of the suspension according to claims 1- 9 in paper deacidification processes, as neutralising agent and also as alkaline reservoir.
- 15) Process for paper deacidification wherein suspensions according to claims 1 - 9 are applied to the papers to be deacidified by: spraying, immersing, brushing, or by mass-deacidification process.
- 16) Use of the suspensions according to Claims 1 – 9 in processes for the consolidation of porous materials.

# INTERNATIONAL SEARCH REPORT

International Application No  
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 D21H25/18		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 D21H		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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<div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.</span> <span><input checked="" type="checkbox"/> Patent family members are listed in annex.</span> </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents:</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*Z* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center;">11 June 2002</div>		Date of mailing of the international search report  <div style="text-align: center;">19/06/2002</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center;">Karlsson, L</div>

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International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

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